

PTO 04-4605

CY=JA DATE=19910312 KIND=A
PN=03-056433

PREPARATION OF DIMETHYLETHER
[Jimechiru Eteru No Seizo Hoho]

Masami Imata, et al.

UNITED STATES PATENT AND TRADEMARK OFFICE
Washington, D.C. August 2004

Translated by: FLS, Inc.

PUBLICATION COUNTRY (19) : JP

DOCUMENT NUMBER (11) : 03056433

DOCUMENT KIND (12) : A

(13) : PUBLISHED UNEXAMINED APPLICATION (Kokai)

PUBLICATION DATE (43) : 19910312

PUBLICATION DATE (45) :

APPLICATION NUMBER (21) : 01188836

APPLICATION DATE (22) : 19890724

ADDITION TO (61) :

INTERNATIONAL CLASSIFICATION (51) : C07C 43/04, 41/09

DOMESTIC CLASSIFICATION (52) :

PRIORITY COUNTRY (33) :

PRIORITY NUMBER (31) :

PRIORITY DATE (32) :

INVENTORS (72) : IMATA, MASAMI; TOKUNO, SHINJI; FUKAYAMA, KANEMITSU; KAGEYAMA, HIROHARU; KARASAWA, MINATO

APPLICANT (71) : MITSUI TOATSU CHEMICALS, INC.

TITLE (54) : PREPARATION OF DIMETHYLETHER

FOREIGN TITLE [54A] : Jimechiru Eteru No Seizo Hoho

SPECIFICATION

1. Title

PREPARATION OF DIMETHYLETHER

2. Claims

Preparation of dimethylether by dehydration of methanol in the presence of a γ -alumina catalyst whose surface area is from 210 to 300 m^2/g , whose pores having a pore radius of less than 300 Å has a volume of from 0.60 to 0.90 mL/g, and whose average pore radius is from 50 to 100 Å.

3. Detailed Description of the Invention

The present invention pertains to a method for preparing dimethylether by dehydration of methanol.

More specifically, it pertains to an improvement of a catalyst used in the process of preparing dimethanol by dehydrating methanol in a gaseous phase.

The demand for dimethylether is increasing as an alternative for chlorofluorocarbons, whose use as aerosol spray materials has become controversial in recent years from the standpoint of environmental pollution.

[Prior Art]

Concerning preparation of dimethylether by dehydration of methanol in the presence of an alumina catalyst, the activities of alumina catalysts having different surface areas are described, for

example, in Journal of Colloid and Interface Science, Vol. 21, pp. 349-357 (1966).

A method for synthesizing dimethylether with the use of large-pore-size alumina catalysts whose average pore radius is from 500 to 1,000 nm is described in JP-A-S59-016845.

[Problems that the Invention Intends to Solve]

With γ -alumina catalysts having a surface area of up to about 220 m^2/g , as those described in the aforesaid document, the initial catalytic activity obtained, for example, under the conditions of 330 $^{\circ}C$ reaction temperature, 10 Kg/cm^2 reaction pressure, and 3,000 h^{-1} space velocity is 75 to 80% in terms of the methanol feed rate [sic] [Translator's note: It should be "conversion rate", judging from the rest of the document] and 99% or higher in terms of the dimethylether selectivity. This initial activity is satisfactory for industrial-scale production, but a study on changes over time reveals that the activity deteriorates in about 1 to 2 months, and the methanol conversion rate drops to near 65 to 70%. For this reason, it is a common practice to increase the reaction temperature to restore the methanol conversion rate.

However, increasing the reaction temperature leads to an increase in the load of an electric heater or combustion furnace that heats a heating medium (that circulates externally) used for heating the reactor. It also causes hydrocarbons, such as methane, ethylene, propylene, etc., carbon monoxide, carbon dioxide, etc., to be

generated as cracked gases; consequently, the selectivity of dimethylether decreases, and the utilization rate of methanol also decreases. This leads to loss of dimethylether in the refining process of dimethylether owing to the need for separating impurities, such as hydrocarbons, etc.

A method that uses γ -alumina catalysts having large-size pores, such as those described in JP-A-S59-016845, for producing dimethylether was developed to further improve the activities of conventional catalysts. However, as pointed out in the report [Kinetica: Kataliz, 2, No. 5, P-859 (1966)] that said the strength of catalysts suddenly drops once their average pore radius exceeds 350 Å, these catalysts having large-size pores have various shortcomings--for example, they have weak mechanical strength, thus requiring meticulous care in handling, and they become powder relatively easily during use.

As explained in the foregoing, conventional γ -alumina catalysts used for production of dimethylether have the shortcoming of poor long-term activity.

This is believed to be caused by a caulking phenomenon, in which, as a catalyst is used over a long period, carbonaceous substances are deposited on the catalyst surface and inside the pores.

To meet the challenge of imparting long-term stability to the catalytic activity, the γ -alumina catalysts having a large pore size, which property is the only difference from conventional catalysts,

described in JP-S59-016845 were developed, but their effects on the aforesaid problems as well as on long-term stability of the catalytic activity are uncertain.

Accordingly, the present invention intends to provide a dimethylether production method that controls the physical properties of the catalyst used for the dehydration reaction of methanol, thereby making it possible to ensure a catalytic activity that is stable for a long period.

[Means for Solving the Problems and Operation]

With the purpose of imparting long-term stability to the activity of γ -alumina catalysts used in production of dimethylether, the present inventors researched extensively about the relationship between the physical properties of γ -alumina catalysts and the long-term stability of their catalytic activity and, as a result, learned that porous γ -alumina catalysts having a specific surface area, pore distribution, and average pore radius exhibit long-term stability. Based on this finding, the inventors researched further and achieved the present invention.

Namely, the present invention relates to preparation of dimethylether by dehydration of methanol in the presence of a γ -alumina catalyst whose surface area is from 210 to 300 m^2/g , whose pores having a pore radius of less than 300 Å has a volume of from 0.60 to 0.90 mL/g, and whose average pore radius is from 50 to 100 Å.

The following explains the present invention in detail.

The porous γ -alumina catalyst pertaining to the present invention can be prepared according the method described in, for example, JP-A-S49-031597, etc.

According to the porous alumina preparation method described in JP-A-S49-031597, amorphous alumina hydrate is, under a weak alkali condition of pH 8 to 12, heated to 50°C or higher and stirred, thereby specially forming pseudo-boehmite having a particle size of 80 Å or larger, after which the alumina hydrate containing this pseudo-boehmite is dried, formed, and further calcined.

The porous γ -alumina catalyst used in the present invention must have a surface area in the range of from 210 to 300 m^2/g , preferably from 230 to 290 m^2/g , a volume of pores having a pore radius of less than 300 Å in the range of from 0.60 to 0.90 mL/g, preferably from 0.62 to 0.85 mL/g, and an average pore radius in the range of from 50 to 100 Å, preferably from 50 to 85 Å.

For producing dimethylether by dehydration of methanol in the presence of the γ -alumina catalyst pertaining to the present invention, it is desirable to carry out the dehydration reaction under the following conditions: the reaction temperature, 200 to 400 °C, preferably 230 to 380°C; the reaction pressure, 1 to 20 Kg/cm^2 , preferably 5 to 15 Kg/cm^2 ; the gas hour space velocity (GHSV), 500 to 10,000 h^{-1} , preferably 1,000 to 5,000 h^{-1} .

The γ -alumina catalyst pertaining to the present invention is usually used in a spherical form, cylindrical form, etc., but it is not limited to these.

The present invention is described in further detail by presenting working examples.

The analysis method employed here was gas chromatography.

Working Example 1

Into a 20 mm-diameter fixed-bed-type stainless steel reactor at the periphery of which was placed an electric furnace, 100 mL of a porous alumina catalyst formed into a 3 mm-diameter spherical shape (surface area: 260 m^2/g ; volume of pores having a pore radius of less than 300 Å: 0.7 mL/g; average pore radius: 54 Å) was charged.

Next, while the reactor periphery temperature was kept at 260°C, methanol gas was fed at a GHSV of 3,000 h^{-1} under a pressure of 10 Kg/cm²G. In this condition, the temperature of the catalyst layer gas at the entrance was 260°C, and the highest temperature of the catalyst layer was 325°C.

The initial reaction result was 82.6% in terms of the methanol conversion rate and 99% or higher in terms of dimethylether selectivity. A catalyst life test was conducted under this condition, thereby obtaining a methanol conversion rate of 74.2% and a dimethylether selectivity of 99% or higher under the same reaction conditions six months later. The results are shown in Table 1.

Working Example 2

Using a porous γ -alumina catalyst (3 mm in diameter, spherical) whose surface area was $210 \text{ m}^2/\text{g}$, whose volume of pores having a pore radius of less than 300 \AA was 0.86 mL/g , and whose average pore radius was 81 \AA , a reaction was carried out with the same equipment and in the same manner as in Working Example 1.

The reactor periphery temperature and the temperature of the catalyst layer gas at the entrance were both at 260°C during the life test period. The obtained results are shown in Table 2.

Working Example 3

Using a porous γ -alumina catalyst (3 mm in diameter, spherical) whose surface area was $230 \text{ m}^2/\text{g}$, whose volume of pores having a pore radius of less than 300 \AA was 0.62 mL/g , and whose average pore radius was 55 \AA , a reaction was carried out with the same equipment and in the same manner as in Working Example 1.

During the life test period, the reactor periphery temperature and the temperature of the catalyst layer gas at the entrance were both at 260°C . The obtained results are shown in Table 3.

TABLE 1

No. of days of operation	Methanol conversion rate (%)	Dimethylether selectivity (%)	Ratio to dimethylether (ppm:Vol)		
			Methane	Other hydrocarbons	CO+CO ₂
1	82.6	>99	115	1.9	130
90	78.1	>99	100	2.0	125
180	74.2	>99	97	2.0	127

TABLE 2

No. of days of operation	Methanol conversion rate (%)	Dimethylether selectivity (%)	Ratio to dimethylether (ppm:Vol)		
			Methane	Other hydrocarbons	CO+CO ₂
1	81.6	>99	113	1.8	128
90	78.3	>99	101	2.0	126
180	75.1	>99	99	1.7	126

TABLE 3

No. of days of operation	Methanol conversion rate (%)	Dimethylether selectivity (%)	Ratio to dimethylether (ppm:Vol)		
			Methane	Other hydrocarbons	CO+CO ₂
1	80.1	>99	109	1.7	135
90	76.5	>99	108	1.6	130
180	72.3	>99	106	1.5	120

Comparative Example 1

Using a commercially available α -alumina catalyst that was in a 1/8 inch x 1/8 inch tablet shape, whose surface area was $175 \text{ m}^2/\text{g}$, whose volume of pores having a pore radius of less than 300 \AA was 0.50 mL/g , and whose average pore radius was 57 \AA , a reaction was carried out with the same equipment and in the same manner as in Working Example 1. The obtained results are shown in Table 4.

As is evident from the results, with the catalyst having a small surface area and a small pore volume, the initial catalytic activity exhibited a tendency to decrease drastically within a half month to one month. After that, when the reaction temperature was increased by 10°C , the reactivity seemed to become relatively stable, but, three months later, the methanol conversion rate dropped to 70 % or less. Even after the reactor peripheral temperature was increased by 10°C , the catalytic activity continued to drop, and it was required to

increase the reactor periphery temperature by 10 °C once every month or thereabouts.

TABLE 4

No. of days of operation	Reactor periphery temperature (C°)	Methanol conversion rate (%)	Dimethylether selectivity (%)	Ratio to dimethylether (ppm:Vol)		
				Methane	Other hydrocarbons	CO+CO ₂
1	260	78.1	>99	210	4.5	260
18	260	72.5	>99	205	4.5	268
19	270	77.4	>99	307	4.8	381
104	270	68.0	>99	296	4.7	388
105	280	74.9	>99	411	9.1	510
131	280	69.2	>99	403	8.7	515
132	290	75.1	>99	457	12.0	602
157	290	68.9	>99	440	13.0	631

[Effects of the Invention]

The dimethylether production method of the present invention controls the physical properties of the γ -alumina catalyst used in the production, thereby realizing an unprecedented catalytic activity having long-term stability, and, along with this, the generation of by-product cracked gases, such as hydrocarbons, carbon monoxide, carbon dioxide, etc., is inhibited, thereby reducing loss of dimethylether in the refining process; thus, the dimethylether production method of the present invention is an industrially excellent method.